THE CHAPMAN-COWLING SECOND APPROXIMATION TO THE VISCOSITY COEFFICIENT OF BINARY GAS MIXTURES

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ABSTRACT The additional bracket integrals needed for the Chapman-Cowling second approximation to the coefficient of viscosity of a binary gas mixture, $[\eta_{mix}]_2$, have been reported The rigorous $[\eta_{mix}]_2$ expression is further simplified where the approximation $M_1 >> M_2$ is valid and also for the case where the additional condition $\sigma_{11} >> \sigma_{22}$ holds Numerical calculations for the specific systems as well as for certain ideal cases have been performed to examine and demonstrate the accuracies of the new formulae derived The maximum contribution of the second approximation for most of the actual systems will be of the order of one per cent.

INTRODUCTION

Recent attempts to measure the transport coefficients to a high degree of precision and their subsequent analysis to determine the intermolecular forces in conjunction with the Chapman-Enskog theory have necessitated the knowledge of more accurate theoretical expressions than were available till a few years back. In the theoretical formulation of Chapman and Cowling (1953) all the transport coefficients are finally represented by an infinite series and the calculation of higher approximations involves only the evaluation of increasing number of terms of this series. In this fashion gaseous diffusion, thermal conductivity and thermal diffusion have already been investigated to some extent, and in the present paper we consider the coefficient of viscosity of a binary mixture, η_{mix}. Only the formulation as given by Chapman and Cowling (1953) will be considered and an alternative treatment according to Kihara (1949) and extended Kihara scheme as given by Mason (1957) will be postponed for the time being till more numerical calculations are performed for the specific systems and its need is realized. It may be pointed out that the accurate determination of viscosity of gaseous mixtures is being pursued in several laboratories and that such data may be used to evaluate the molecular potentials is indicated by Hirschfelder, Taylor, Kihara and Rutherford (1961) Srivastava (1961) has already used some viscosity data to determine the unlike interactions of several gas pairs. For an accurate interpretation of all these works the analysis of higher approximations will be essential. In this paper we give the expression for the second

approximation to η_{mix} and discuss results for the Ar-He and He-Xe systems in detai land a few other cases of interest.

EVALUATION OF BRACKET INTEGRALS

The determination of higher approximations to transport coefficients according to the procedure of Chapman and Cowling (1953) essentially involves the evaluation of a set of bracket integrals. The details of this calculation are given by Chapman and Cowling (1953) and will not be repeated here. Some of these bracket integrals have been evaluated by Chapman and Cowling (1953), and by Mason (1954, 1957). The additional integrals needed for the second approximation to η_{mix} are listed below

$$\left[S_{\frac{5}{2}}^{(1)}(C_1^2)\mathbf{C}^0{}_1\mathbf{C}_1,\ \mathbf{C}^0{}_2\mathbf{C}_2\right]_{12} = -\frac{4M_1M_2^2}{3(M_1+M_2)^3}$$
$$[70\Omega_{12}^{(1,1)} - 28\Omega_{12}^{(1,2)} - 21\Omega_{12}^{(2,2)} + 6\Omega_{12}^{(2,3)}],$$

$$\left[\mathbf{C}_1{}^0\mathbf{C}_1,\ S_{\frac{5}{2}}^{(1)}(C^2{}_2)\mathbf{C}^0{}_2\mathbf{C}_2\right]_{12} = -\frac{4M_1{}^2M_2}{3(M_1+M_2)^3}$$
$$[70\Omega_{12}^{(1,1)} - 28\Omega_{12}^{(1,2)} - 21\Omega_{12}^{(2,2)} + 6\Omega_{12}^{(2,3)}],$$

$$\left[S_{\frac{5}{2}}^{(1)}(C^2{}_1)\mathbf{C}^0{}_1\mathbf{C}_1,\ S_{\frac{5}{2}}^{(1)}(C^2{}_2)\mathbf{C}^0{}_2\mathbf{C}_2\right]_{12} = -\frac{2M^2{}_1M^2{}_2}{3(M_1+M_2)^4}$$
$$[770\Omega_{12}^{(1,1)} - 392\Omega_{12}^{(1,2)} - 301\Omega_{12}^{(2,2)} + 64\Omega_{12}^{(1,3)} + 84\Omega_{12}^{(2,3)} - 12\Omega_{12}^{(2,4)} + 24\Omega_{12}^{(3,3)}],$$

$$\left[S_{\frac{5}{2}}^{(1)}(C^2{}_1)\mathbf{C}^0{}_1\mathbf{C}_1,\ \mathbf{C}^0{}_1\mathbf{C}_1\right]_{12} = \frac{4M^2{}_2}{3(M_1+M_2)^3}$$
$$[70M_1\Omega_{12}^{(1,1)} - 28M_1\Omega_{12}^{(1,2)} + 21M_2\Omega_{12}^{(2,2)} - 6M_2\Omega_{12}^{(2,3)}],$$

$$\left[S_{\frac{5}{2}}^{(1)}(C^2{}_1)\mathbf{C}^0{}_1\mathbf{C}_1,\ S_{\frac{5}{2}}^{(1)}(C^2{}_1)\mathbf{C}^0{}_1\mathbf{C}_1\right]_{12} = \frac{2M_2}{3(M_1+M_2)^4}$$
$$[2M_1(140M^2{}_1 + 245M^2{}_2)\Omega_{12}^{(1,1)} - 392M_1M^2{}_2\Omega_{12}^{(1,2)} + 64M_1M^2{}_2\Omega_{12}^{(1,3)}$$
$$+ (154M^2{}_1M_2 + 147M^3{}_2)\Omega_{12}^{(2,2)} - 84M^3{}_2\Omega_{12}^{(2,3)} + 12M^3{}_2\Omega_{12}^{(2,4)}$$
$$+ 24M_1M^2{}_2\Omega_{12}^{(3,3)}].$$

Here the bold letters refer to vector quantities, $\Omega_{l,j}^{(l,n)}$ are the Chapman-Cowling collision integrals, M_1 and M_2 are the molecular weights of species 1 and 2 respectively, and rest of the quantities are as defined by Chapman and Cowling (1953).

THEORETICAL FORMULAE FOR VISCOSITY

According to Chapman and Cowling (1953) the coefficient of viscosity of a binary gas mixture, η_{mix}, is given by

$$\eta_{mix} = \tfrac{5}{2}kT\ Lt_{m\to\infty}\left[X^2{}_1B_{11}^{(m)} - 2X_1X_2B_{1-1}^{(m)} + X^2{}_2B_{-1-1}^{(m)}\right] \Big/ X_1X_2B^{(m)}, \quad \ldots \quad (1)$$

where X_i is the mole fraction of the species i, k is the Boltzmann's constant, T is the temperature of the gas mixture, $B^{(m)}$ is a symmetrical determinant of order $2m$, whose general term is b_{ij}, where i and j range from $-m$ to $+m$, excluding zero, the minor of $B^{(m)}$ obtained by suppressing the row and column containing b_{ij} is denoted by $B_{ij}^{(m)}$ The determinant elements b_{ij} necessary for the first approximation, $m = 1$ in Eq. (1) usually denoted by $[\eta_{m12}]_1$, are already given by Chapman and Cowling (1953). Now a days it is more common to use the reduced collision integrals, $\Omega_{ij}^{(l,m)*}$ which are defined as the ratio of $\Omega_{ij}^{(l,m)}$ to its value for the rigid sphere model, Hirschfelder, Curtiss and Bird (1954). In this notation Eq (1) becomes

$$\eta_{m12} = \frac{RT}{2N\sigma_{12}^2}\left(\frac{RT}{2\pi}\right)^{\frac{1}{2}}\left(\frac{M_1M_2}{M_1+M_2}\right)^{\frac{1}{2}} \underset{m\to\infty}{Lt} [X_1^2 B_{11}^{(m)} - 2X_1X_2B_{1-1}^{(m)} + X_2^2 B_{-1-1}^{(m)}]/[X_1X_2B^{(m)}] \tag{2}$$

where N is the Avogadro's number, R is the gas constant per mole, σ_{12} is a distance parameter characteristic of the interaction between two molecules of types 1 and 2, and its exact definition follows from the particular form chosen for the intermolecular potential. $B^{(m)}$ and $B_{ij}^{(m)}$ are again defined in the same fashion as in connection with Eq. (1) except that b_{ij} are now defined differently. The Eq. (2) quoted by Mason (1957) contains a misprint.

The calculation of η_{m12}, according to Eq. (2), requires the knowledge of determinants, $B^{(m)}$, $B^{(m)}_{11}$, $B^{(m)}_{1-1}$, $B^{(m)}_{-1-1}$ and hence the determinant elements, b_{ij}. The additional b_{ij} needed for the second approximation $m = 2$, in Eqs (1) and (2) usually denoted by $[\eta_{m12}]_2$, have been evaluated by Saxena and Joshi (1963) and will not be reproduced here because of their length.

The formula for $[\eta_{m12}]_2$ can be simplified for certain limiting cases of binary gas mixtures. The systems where either of the components is present in small concentration is not very interesting because then the system reduces to the case of a pure gas for which the contribution of higher approximations is known. The case when $M_1 >> M_2$, so that higher powers of $M = (M_2/M_1)$ are negligible, is interesting. Much simpler expressions for the four determinants of Eq. (2) are obtained if these determinants are expanded and only those terms are retained which contain the explicit power of M smaller than two. The simpler expressions are

$$B^{(2)} = (b_{11}b_{22} - b^2_{12})(b_{-1-1}b_{-2-2} - b^2_{-1-2}), \tag{3}$$

$$B_{11}^{(2)} = b_{22}(b_{-1-1}b_{-2-2} - b^2_{-1-2}), \tag{4}$$

$$B^{(2)}_{1-1} = b_{22}(b_{1-1}b_{-2-2} - b_{1-2}\,b_{-1-2}), \tag{5}$$

$$B^{(2)}_{-1-1} = b_{-2-2}(b_{11}\,b_{22} - b_{12}^2). \tag{6}$$

If the additional condition $\sigma_{11} >\!\!> \sigma_{22}$ holds, so that terms containing σ_{22}/σ_{11} are negligible, the above expressions get further simplified The final results are

$$B^{(2)} = \{(b'_{11}+(X_1/X_2)B''_{11})(b'_{22}+(X_1/X_2)B''_{22})-(b'_{12}+(X_1/X_2)B''_{12})^2\}$$
$$(b_{-1-1}b'_{-2-2}-b'^2_{-1-2}), \quad \ldots \quad (7)$$

$$B^{(2)}_{11} = (b'_{22}+(X_1/X_2)B''_{22})(b'_{-1-1}b'_{-2-2}-b'^2_{-1-2}), \quad \ldots \quad (8)$$

$$B^{(2)}_{1-1} = (b'_{22}+(X_1/X_2)B''_{22})(b'_{-11}b'_{-22}-b''_{-1-2}b_{21}), \quad \ldots \quad (9)$$

$$B^{(2)}_{-1-1} = b'_{-2-2}\{(b'_{11}+(X_1/X_2)B''_{11})(b'_{22}+(X_1/X_2)B_{22}'')$$
$$(b'_{12}+(X_1/X_2)B_{12}'')^2\} \quad \ldots \quad (10)$$

B_{ij}'' are obtained from corresponding b_{ij} by substituting $\sigma_{11} = 2\sigma_{12}$

Even for those systems where M is not sufficiently small fairly accurate values of $[\eta_{mix}]_2$ can be obtained from the above equations if Eq (3) is replaced by the following

$$B^{(2)} = (b_{11}b_{22}-b_{12}^2)(b_{-1-1}b_{-2-2}-b^2_{-1-2})-b_{22}(b_{-2-2}b^2_{1\,1}$$
$$+b_{-1-1}b^2_{1\,2})-b_{11}(b_{2\,2}b^2_{-12}+b^2_{-1\,-1}b_{2-2}). \quad \ldots \quad (11)$$

The additional terms in Eq. (11) arise from those elements of the Chapman-Cowling determinant, $B^{(2)}$, which contain the product of two diagonal terms. Such terms do not occur in Eqs (4) to (6) which therefore remain unaltered This procedure has also proved very successful in improving the accuracies of the simpler formulae for the Chapman-Cowling second approximation to the thermal diffusion factor of the binary gas mixtures, Saxena and Joshi (1963a, 1963b)

RESULTS AND DISCUSSION

Sample calculations were first performed to estimate the accuracy of the approximate formulae derived in the previous section. It was found that for values of $M < (1/30)$ the approximate formula, Eq. (2) in conjunction with Eqs. (3) to (6), yield fairly accurate values Thus, for the He—Xe system the rigorous and approximate second approximation values differ only by 0.037%, while the difference between the values of the first two approximations of η_{mix} is 1 6%. This calculation was done according to the rigid sphere model and it was assumed that $\sigma_{11}/\sigma_{12} = 1.387$ and $X_1/X_2 = 10$. For systems where $M > (1/30)$ it was found essential to replace Eq. (3) by Eq. (11). Computed values of η_{mix} for the specific case of He-Ar are given in the Table I. It is seen that the maximum difference between the approximate and rigorous $[\eta_{mix}]_2$ values is 0.09% Equation (2) in conjunction with Eqs (7) to (10) is also quite accurate if $\sigma_{11} >\!\!> \sigma_{22}$. Under this condition and on the rigid sphere model for $M = (1/30)$ the approximate $[\eta_{mix}]_2$ value differs from the rigorous value only by 0 03%, while the second approximation value is 2.8% greater than the first approximation value

In general, the difference between the first and second approximations to η_{mix} will depend upon the temperature, composition, on the nature of the intermolecular potential and will differ from system to system. For the He-Ar system on the rigid sphere model if it is assumed that $(\sigma_{11}/\sigma_{12}) = 1$ we find that the percentage difference between the first two approximations is 1.2 when $X_1/X_2 = 10$, and 0.9 when $X_1/X_2 = 1$. The calculations reported in the Table I for this system on a realistic modified Buckingham exp - six potential in conjunction with the potential parameters given by Mason (1955), reveal that the maximum contribution of the second approximation is only 0.6%. The contribution of the second approximation will usually reduce as M reduces. Thus, when M is reduced from (1/30) to 10^{-10} the contribution of second approximation falls from 2.8 to 1.5%, for the rigid sphere model and with the assumption that $\sigma_{22} = \sigma_{11}$.

To see the dependence on composition we consider the experimental data of Rietveld, Utterbeck and Van Den Berg (1953) for He-Ar system at $T = 291.1°K$. These data are listed in the Table I and involve the experimental uncertainty of about 1%. It is seen from this table that the difference between the first and second approximations does not vary much with the composition though it exhibits an increase as the proportion of the lighter component increases in the mixture. Thus, though the contribution of the second approximation is comparatively small yet its knowledge is essential in view of the high precision (~ 0.1%) attainable in the measurements of viscosity, Kestin and Leidenfrost (1959).

Another point to note in Table I is that consideration of higher approximation to η_{mix} mostly improves the agreement between theory and experiment. Further, the theoretical values of η_{mix} according to the exp-six potential are in better agreement with the experiment than the calculated values of Rietveld *et al.* (1953) on the familiar Lennard-Jones (12-6) potential. This again tends to simply confirm the earlier view of Weissman, Saxena and Mason (1960) that the exp-six is a better potential for He-Ar system than L—J (12-6) potential.

It will also be interesting to examine the contribution of the second approximation at still higher temperatures. To investigate this we choose He-Xe system for which Chapman-Enskog theory holds rigorously and the two molecules are widely different. The calculations have been performed according to L—J(12-6) potential and using the Eqs (2) to (6). The potential parameters for He ($\epsilon/k = 10.22°K$, $\sigma = 2.556Å$) as given by Hirschfelder, Curtiss and Bird (1954), and for X_i of Whalley and Schneider (1955) were used. The reason for choosing this particular set for X_i lies in its ability to correlate all the observed properties as shown by Saxena and Joshi (1963a). The parameters for the unlike interaction were computed by the conventional combination rules viz., geometric mean rule for ϵ_{12} and arithmetic mean rule for σ_{12}. The final results are tabulated in Table II. The contribution of the second approximation increases with temperature and also with the increasing percentage of the lighter component.

TABLE I

Experimental and calculated values of η_{mix} in μP for He-Ar system at $T = 291.1°K$ as a function of composition

% He	η_{mix} Exptl	Theoretical	η_{mix} values		Percentage deviation	
		$[\eta_{mix}]_1^{Theo}$	$[\eta_{mix}]_2^{Theo}$	$[\eta_{mix}]_2^{adjusted}$ *	Columns 3 and 4	Columns 4 and 5
11.4	222.3	221.48	222.0	222.06	0.2	0.03
13.65	224.3	223.27	223.93	223.98	0.3	0.02
20.1	224.0	223.40	224.05	224.10	0.3	0.02
29.2	228.1	225.32	225.99	226.08	0.3	0.04
38.2	229.4	226.83	227.77	227.66	0.4	0.05
51.0	230.9	228.27	229.27	229.34	0.5	0.03
53.9	231.1	228.45	229.63	229.49	0.5	0.06
59.4	230.4	228.34	229.38	229.40	0.4	0.01
70.2	229.0	226.58	227.62	227.75	0.4	0.06
80.4	222.9	221.56	222.68	222.85	0.5	0.08
89.7	210.1	211.97	213.30	213.51	0.6	0.09

*Values obtained from eqn. (2) in conjunction with eqns. (4) to (6) and (11)

TABLE II

The ratio $[\eta_{mix}]_2/[\eta_{mix}]_1$ for the He-Xe system at various temperatures and and composition on L—J(12 · 6) potential

% X_2 \ T °K	300	600	1000
0.0001	1.0078	1.0077	1.0076
25	1.0067	1.0077	1.0083
50	1.0058	1.0066	1.0077
75	1.0023	1.0058	1.0065
99.9999	1.0002	1.0027	1.0050

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